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(71)Applicant : TORAY IND INC

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(72)Inventor : TANAKA HIROYUKI
NIINUMADATE HIROSHI
MATSUI RYOSUKE

(54) WHITE ALIPHATIC POLYESTER FILM AND PRODUCTION METHOD THEREFOR

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a white aliphatic polyester film excellent in opacifying power, writing ability and scratch resistance, and useful as a display substrate for printing or writing, especially a carbon copying slip.

SOLUTION: The white aliphatic polyester film comprises 60 to 95 wt.% aliphatic polyester and 5 to 40 wt.% inorganic particles, and has ≥ 0.4 optical density and $\geq 75\%$ whiteness.

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CLAIMS

[Claim(s)]

[Claim 1]A white aliphatic polyester film which contains an inorganic particle for aliphatic polyester five to 40% of the weight 60 to 95% of the weight, and is characterized by optical density's being 0.4 or more and a whiteness degree being not less than 75%.

[Claim 2]The white aliphatic polyester film according to claim 1, wherein an inorganic particle is at least one sort in titanium oxide, calcium carbonate, and barium sulfate.

[Claim 3]The white aliphatic polyester film according to claim 1 or 2, wherein aliphatic polyester is polylactic acid system polyester.

[Claim 4]The white aliphatic polyester film according to any one of claims 1 to 3, wherein thickness of a film is 10-100 micrometers.

[Claim 5]The white aliphatic polyester film according to any one of claims 1 to 4, wherein apparent specific gravity is 1.15 - 1.30 g/cm³.

[Claim 6]The white aliphatic polyester film according to any one of claims 1 to 5, wherein a degree of brilliancy of at least one side is 50% or less.

[Claim 7]The white aliphatic polyester film according to any one of claims 1 to 6 which consists of two-layer at least and is characterized by inorganic particle content of at least one surface being 5% of the weight or more less than inorganic particle content of the whole film.

[Claim 8]The white aliphatic polyester film according to any one of claims 1 to 7 using for carbon copy checks.

[Claim 9]An aliphatic series polyester chip which contains an inorganic particle 20 to 50% of the weight, A manufacturing method of the white aliphatic polyester film according to any one of claims 1 to 8, wherein content of an inorganic particle mixes an aliphatic series polyester chip which is 5 or less % of the weight and extends melt extruding and an obtained unstretched film in the at least 1 direction.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a white aliphatic polyester film. Especially, in detail, concealment nature, note nature, and a sex with a crack-proof are especially good, and a carbon copy check etc. are related with an aliphatic polyester film useful as a display base material which performs printing and a note, and a manufacturing method for the same.

[0002]

[Description of the Prior Art]As a white film which contains a detailed cave inside, conventionally, To polyethylene terephthalate resin, inorganic particles, such as titanium oxide and calcium carbonate, After carrying out mixed film production of the resin immiscible to polyethylene terephthalate resin, the method of making the detailed cave which extended to 2 shaft orientations and used an inorganic particle and immiscible resin as the core form is known, and it is used for a television film, a label, etc. However, such a white film currently used from the former will remain in the ground or underground semipermanently, when it is neglected after use or flaking processing is carried out into the ground, since it did not decompose under natural environment, or catabolic rate is very low. When sea dumping is carried out, a scene is spoiled or the living environment of a marine organism is destroyed. When incineration processing is carried out, waste treatment serves as a social problem with expansion of consumption of promoting degradation of an incinerator etc. with the high combustion heat. On the other hand, when aliphatic polyester films including polylactic acid are discarded by natural environment, they are disassembled, For example, as a white film which consists of polylactic acid which is developed considering becoming a harmless decomposition product as a feature, and has biodegradability by a microorganism after hydrolyzing automatically in soil, the film which added resin immiscible to polylactic acid is proposed -- **** (JP,2002-146071,A) -- since a film surface becomes smooth too much in such a white film, it is inferior to note nature with a pencil or a pen. Since an additive was soft resin, when a metal guide etc. were touched within a film production process or a post-processing process, there was a problem of being easy to generate a film crack.

[0003]

[Problem(s) to be Solved by the Invention]This invention relates to a white aliphatic polyester film which was compatible in concealment nature, note nature, and abrasion resistance, and a manufacturing method for the same, in order to solve this technical problem.

[0004]

[Means for Solving the Problem]In order [which attains an aforementioned problem] to carry out, a white aliphatic polyester film of this invention mainly has the next composition. That is, it is a white aliphatic polyester film which contains an inorganic particle for aliphatic polyester five to 40% of the weight 60 to 95% of the weight, and is characterized by optical density's being 0.4 or more and a whiteness degree being not less than 75%.

[0005]A manufacturing method of a white aliphatic polyester film of this invention mainly has the next composition. Namely, an aliphatic series polyester chip which contains an inorganic particle 20 to 50% of the weight, It is a manufacturing method of the white aliphatic polyester film according to any one of claims 1 to 8, wherein content of an inorganic particle mixes an aliphatic series polyester chip which is 5 or less % of the weight and extends melt extruding and an obtained unstretched film in the at least 1 direction.

[0006]

[Embodiment of the Invention]General formula-O-CHR-CO- (R is hydrogen or an alkyl group of the carbon numbers 1-3) is made aliphatic polyester in this invention with a main repeating unit. As such aliphatic polyester, although polylactic acid, polyglycolic acid, poly (2-oxybutanoic acid), etc. can be mentioned, for example, it is not limited to these. Although these aliphatic polyester may be used independently, it does not matter even if it uses two or more kinds of mixtures, and a copolymer. Although optical isomers, such as L-object, DL-object, and D-object, exist, those any may be sufficient as the thing which has asymmetrical carbon in polymer, and the mixture of these isomers may be sufficient as it. The polymer used as the raw material of these films mentioned above is manufactured by publicly known methods, such as carrying out ring opening polymerization of the corresponding drying cyclic ester compound of alpha-oxy acid.

[0007]In the above-mentioned aliphatic polyester, polylactic acid system polyester is the most preferred. If the polylactic acid system polyester said here is the copolymers of polylactic acid or lactic acid, and other hydroxycarboxylic acid, or these mixtures and is a range which does not check the purpose of this invention, it is the purpose of adjusting handling nature, processability, and physical properties, Additive agents, such as a plasticizer, lubricant, a thermostabilizer, coloration inhibitor, an ultraviolet ray absorbent, light stabilizer, and an antioxidant, may be made to contain. As lactic acid, L-lactic acid and D-lactic acid are mentioned and glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyrate, 4-hydroxyvaleric acid, 5-hydroxyvaleric acid, and 6-hydroxycaproic acid are mentioned as other hydroxycarboxylic acid.

[0008]The white aliphatic polyester film of this invention contains an inorganic particle for the above-mentioned aliphatic polyester 15 to 30% of the weight preferably five to 40% of the weight 70 to 85% of the weight 60 to 95% of the weight. There is less aliphatic polyester content than 60 % of the weight, or when there is more content of an inorganic particle than 40 % of the weight, Since it becomes difficult to obtain a uniform film by condensation of an inorganic particle, it becomes a film inferior to ductility and an inorganic particle drops out easily, it becomes easy to generate the dirt by omission particles at the cap, film production process, and post-processing process at the time of melting extrusion. On the other hand, there is more aliphatic polyester content than 95 % of the weight, or when there is less content of an inorganic particle than 5 % of the weight, Since good concealment nature and note nature cannot be attained and it becomes easy to delete a film, there is a problem of becoming easy to generate a film crack within a film production process and the process of post processing.

[0009]Although titanium oxide, calcium carbonate, barium sulfate, talc, a silica particle, etc. can be used for the inorganic particle used for the white polyester film of this invention, In order to obtain the film which has a desirable whiteness degree and optical density, titanium oxide, calcium carbonate, and barium sulfate are preferred, and especially titanium oxide is preferred. As for the mean particle diameter of an inorganic particle, 0.1-5 micrometers is preferred.

[0010]When using titanium oxide for the white polyester film of this invention, can use anything of an anatase type, rutile type, and bull kite type crystal form, but. In order for the dispersibility in the inside of aliphatic polyester and the whiteness degree of a film to obtain a good film, It is preferred to use titanium oxide of an anatase type or a rutile type, and it is preferred to cover the surface with oxides, such as alumina and silica, in order to raise the dispersibility in aliphatic polyester, or to use what performed the surface treatment by aliphatic series polyol etc.

[0011]When using a calcium carbonate particle for the white polyester film of this invention, anything of a calcite type, an aragonite type, and a vaterite type crystal form can be used.

[0012]When using barium carbonate particles for the white polyester film of this invention, it is preferred to use the precipitated barium sulphate manufactured by the chemical reaction from baryte.

[0013]To the white polyester film of this invention, 5 or less % of the weight of thermoplastics and a plasticizer can be added in the range which does not check the purpose of this invention. Since it becomes easy to attain a desirable whiteness degree, it is effective to add polyolefines, such as polyethylene terephthalate, the copolymerized polyester, polypropylene, in the range less than 5 % of the weight.

[0014]The field of concealment nature to the optical density of the white aliphatic polyester film of this invention needs to be 0.8 or more preferably 0.6 or more. Optical density becomes insufficient [concealment nature] by less than 0.6. Although the maximum in particular of optical density is not limited, it is difficult to use 1.50 or more in the 50-micrometer terms in thickness of a film generally.

[0015]The white aliphatic polyester film of this invention requires that the field of the clear nature of printing or a note to a whiteness degree should be not less than 85% preferably not less than 75%. When a whiteness degree is smaller than 75%, it will become what is inferior in the clearness at the time of writing down with a black and blue pencil and pen.

[0016]As for the thickness of the white aliphatic polyester film of this invention, 20-100 micrometers is preferred from the loss in quantity at the time of using as a label, and the field of a weight saving, and its 25-50 micrometers are especially preferred. The carbon copy nature at the time of using that it is a desirable range which requires thickness as a carbon copy check becomes good especially.

[0017]As for the white aliphatic polyester film of this invention, it is preferred that the degree of brilliancy of at least the field of note nature to one side is 40% or less. It can be considered as the film which was excellent in especially note nature in it being a desirable range which requires a degree of brilliancy.

[0018]As for the white aliphatic polyester film of this invention, it is preferred that apparent specific gravity is $1.15-1.35\text{g/cm}^3$, and also $1.25-1.35$. While it can do with the film which was excellent in note nature in it being a desirable range which requires apparent specific gravity, it is hard to generate a tear within a film production process, and since abrasion resistance is good, it is hard to generate the process dirt by omission of an inorganic particle at a film production process or the process of post processing.

[0019]In order to attain good abrasion resistance, the white aliphatic polyester film of this invention is used

as the film more than two-layer at least, and it is preferred that the inorganic particle content of at least one surface is 5% of the weight or more less than the inorganic particle content of the whole film. When severe abrasion resistance is required at a post-processing process, especially the thing to consider as 3 lamination which laminated the inorganic particle low concentration contained layer to both sides of the high concentration contained layer is preferred. 1-5 micrometers of lamination thickness of an inorganic particle low concentration contained layer are 1-3 micrometers especially preferably.

[0020]Next, the manufacturing method of the white aliphatic polyester film of this invention is explained. In the manufacturing method of this invention, melting extrusion of the aliphatic series polyester chip which contains an inorganic particle 20 to 50% of the weight, and the aliphatic series polyester chip whose content of an inorganic particle is 5 or less % of the weight is mixed and carried out. Thus, if what is called a masterbatch method that mixes and carries out melting extrusion of the aliphatic series polyester chip from which the content of an inorganic particle differs is not adopted, it is homogeneous and neither cap dirt nor a film with little process dirt generating can be obtained efficiently.

[0021]In the manufacturing method of this invention, the unstretched film produced by carrying out as above-mentioned is extended in the at least 1 direction. If it does not extend in the at least 1 direction, film strength runs short practically.

[0022]Although the white aliphatic polyester film of this invention can be obtained with a tubular film process, a simultaneous biaxial-stretching method, and the manufacturing method of the oriented film of existing one by one, such as a biaxial-stretching method, its biaxial-stretching method is preferred one by one from the ability to make film production speed high-speed. In manufacture of the white aliphatic polyester film of this invention in a biaxial-stretching method one by one, Blend the aliphatic series polyester chip containing many above-mentioned inorganic particles first dry under the vacuum, and the aliphatic series polyester chip which contained the inorganic particle few, and an extrusion machine is supplied, By a publicly known method, a sheet shaped is stuck to melting extrusion and a casting drum, cooling solidification is carried out to it from a slit shape cap, and an unstretched film is obtained. When providing the layer which contained the inorganic particle few in the surface of a film, the combined extrusion which makes melting polymer join in the upper stream of a cap within a cap, and obtains a lamination unstretched film using two or more sets of extrusion machines is the most preferred. It is preferred to extend continuously the unstretched film obtained by this method to one way at least, and also to extend to direction crossing at a right angle, and to improve adhesion with the substrate of a thin film layer and the tough nature of a thin film layer by heat-treating. It is preferred that the roll extension which used the peripheral speed difference of the heating roller for extension of the direction of a film length hand uses for heat treatment after extension and biaxial stretching of a film width direction the tenter which has a continuation clip.

[0023]The white aliphatic polyester film of this invention, The stratum functionale by coating may be provided for the purpose of giving adhesion, antistatic property, etc. with adhesives for pasting together to ink or other raw materials, The in-line coating method performed within the manufacturing process of a white aliphatic polyester film and the off-line coating method performed after rolling up of a white aliphatic polyester film can be used.

[0024]Although the white aliphatic polyester film of this invention can be used for various uses as which concealment nature and white nature are required, it can be preferably used for the label use which

performs especially printing and a note, especially the checks which perform a carbon copy.

[0025]

[Example] Hereafter, an example explains this invention further. Although especially explained taking the case of the polylactic acid which is typical aliphatic polyester, of course, this invention is not limited to this.

[A measuring method of the characteristic]

(1) The transmittance factor density in one film was measured using optical density Macbeth optical density meter TR927. Optical density serves as an index of concealment nature.

(2) Whiteness degree (%)

L, a, and b value were calculated using spectrum type color difference meter SE-2000 (made by Nippon Denshoku Industries Co., Ltd.), and it asked for the whiteness degree using the lower type in accordance with the JIS L 1015 C method.

[0026] Whiteness degree = $[(\%)] 100 - (100 - L)^2 + a^2 + b^2)^{1/2}$ (3) specific-gravity film was cut to 50 mm x 60 mm, and it measured with the underwater substitution method using high precision electronic hydrometer SD-120L (product made from Mirage Trade), and asked for specific gravity.

(4) Degree of brilliancy (%)

In accordance with the method specified to JIS K 7105, it measured using Suga Test Instruments digital deflection glossmeter UGV-5D. The specular gloss which is a rate of the surface regular reflection light to the beam of light which entered at the angle of 60 degrees was measured.

(5) Although the pencil of the hardness B can be used for a note nature film surface, ten straight lines 10 cm in length can be drawn at intervals of 3 mm under a 200g load, ten straight lines can be checked visually and ten straight lines can check the case where there is no skip, by A and viewing, The case where ten straight lines could not check the case where there is a skip, by good and viewing was made poor.

(6) Although the case where Kokuyo Co., Ltd. make carbonic-paper 1300-K1 is inserted for a carbon copy nature film between a five-sheet pile and each, and notes of a character is taken with a ball-point, and that of the character which does not have a skip in the bottom film surface can be taken can be transferred to A and the bottom, The case where good and transfer of the 5th sheet could not check visually the case where a skip arises was made poor.

(7) What carried out the slit of a sex with a crack-proof, the process dirt characteristic, and the sex film with a crack-proof to 1/2-inch-wide tape shape is run the guide pin (surface-roughness Ra: 100 nm) top made from stainless steel using a tape running testing machine (the contact angle of 90 degrees and the tension of 100 g by travel-speed/of 2 m). Run 100 mm in length, the 50 number of times of a run.

[0027] At this time, the crack included in a film was observed under the microscope, and, as for less than five per tape width, the crack not less than 10 micrometers wide judged with good and less than ten 10 [A and / five or more] or more being poor.

- Although the case depended on film **** of the process dirt characteristic and the shape made from stainless steel of a guide pin after a 50 times run where it could delete, the state of powder was judged visually and white powder has adhered all over the guide pin surface can be deleted by a defect and viewing and powder can be checked, When adhesion area was 5% or less on the surface of a guide pin, the case where it could delete by good and viewing and powder could not be checked was made into A.

(Preparation of aliphatic polyester resin)

Aliphatic-polyester-resin A: L-poly(lactic acid (melting point of 170 °C)) of the weight average molecular weight 200,000 [about] was used.

Aliphatic-polyester-resin B: To aliphatic-polyester-resin A, titanium oxide (Ishihara Sangyo Kaisha, Ltd. make TIPAQUE CR60-1) was kneaded at 200 °C using the publicly known twin screw extruder, and it was considered as the master pellets of 40 % of the weight of titanium oxide concentration.

Aliphatic-polyester-resin C: To aliphatic-polyester-resin A, the calcium carbonate particle (Japanese east powdering NCC45 made from Industry) was kneaded at 200 °C using the publicly known twin screw extruder, and it was considered as the master pellets of 15 % of the weight of calcium carbonate concentration.

Under a vacuum and 120 °C conditions, it dried for 5 hours and the example 1 aliphatic-polyester-resin chip was used, respectively. Aliphatic-polyester-resin A and aliphatic-polyester-resin B are blended by a weight ratio 5:3, What was mixed so that inorganic particle content might be 15 % of the weight was supplied to the extrusion machine, it extruded to film state at the T-die cap temperature of 200 °C, the cast was carried out to drum lifting cooled at 25 °C, and the unstretched film was produced. Grasp after 3 time ***** and an uniaxial stretched film with a clip to a longitudinal direction between 75 °C heating rollers continuously, and it leads in a tenter, It extended 3.5 times in the transverse direction, heating at the temperature of 80 °C, 140 °C and heat treatment for 10 seconds were performed in the state where it fixed crosswise, and the 50-micrometer-thick white aliphatic polyester film was obtained. The weighted solidity of the obtained film was good as it was shown in Table 1.

[0028]

[Table 1]

【表 1】

N o.	無機粒子含有量 (重量%)	光学濃度	白色度 (%)	比重 (g/cm ³)	光沢度 (%)	筆記性	カーボン 複写性	耐傷付き性	工程汚 れ特性
実施例 1	15	0.80	89	1.30	38	優	良	優	良
実施例 2	10	0.65	83	1.28	50	良	優	良	良
実施例 3	15	0.75	95	1.20	38	良	良	優	良
実施例 4	5	1.05	85	1.32	80	良	良	優	優
比較例 1	4	0.90	80	1.20	88	不良	不良	不良	良
比較例 2	5	0.15	51	1.24	120	不良	不良	不良	良
比較例 3	0	0.55	95	0.70	110	不良	不良	不良	良

Example 2 aliphatic-polyester-resin A and aliphatic-polyester-resin B were set to 3:1 by the weight ratio, it mixed so that inorganic particle content might be 10 % of the weight, and the white aliphatic polyester film was obtained like Example 1 except having changed film production speed and film thickness having been 25 micrometers. The weighted solidity of the obtained film was good as it was shown in Table 1.

The white aliphatic polyester film was obtained like Example 1 except having used example 3 aliphatic-polyester-resin C independently. The weighted solidity of the obtained film was good as it was shown in Table 1.

Using the extrusion machine of 42 examples, a main stratum mixes aliphatic-polyester-resin A and aliphatic-polyester-resin B by a weight ratio 1:1, and makes inorganic particle content 20 % of the weight, The sublayer mixed aliphatic-polyester-resin A and aliphatic-polyester-resin B by the weight ratio 7:1, made inorganic particle content 5 % of the weight, and obtained the white aliphatic polyester film like Example 1 except having laminated the sublayer so that it might be with the last film and might become a thickness of 3 micrometers to both sides of a main stratum, respectively. The weighted solidity of the obtained film was good as it was shown in Table 1.

Comparative example 1 aliphatic-polyester-resin A and aliphatic-polyester-resin B were set to 9:1 by the weight ratio, it mixed so that inorganic particle content might be 4 % of the weight, and the white aliphatic polyester film was obtained like Example 1 except having changed film production speed and film thickness having been 150 micrometers. As Table 1, since thickness was large, optical density and a whiteness degree were good, but the weighted solidity of the obtained film is inferior to note nature, carbon copy nature, and a sex with a crack-proof.

To comparative example 2 twin screw extruder, composite supply of the silica particle (SAIRISHIA made from Fuji SHIRISHIA Chemicals) was directly carried out to aliphatic-polyester-resin A, and the aliphatic polyester film was obtained like Example 1 except having carried out inorganic particle content and film thickness having been 25 micrometers 5% of the weight. The weighted solidity of the obtained film does not fill optical density, but is inferior to note nature, carbon copy nature, and a sex with a crack-proof as it is shown in Table 1.

To comparative example 3 twin screw extruder, the aliphatic polyester film was obtained like Example 1 except having mixed and supplied aliphatic-polyester-resin A and polyethylene terephthalate isophthalate copolymerized polyester (the rate of isophthalic-acid copolymerization: 17-mol %) to 9:1 by the weight ratio. Optical density and a whiteness degree are good as the weighted solidity of the obtained film is shown in Table 1, but since an inorganic particle is not contained, it is inferior to note nature, carbon copy nature, and a sex with a crack-proof.

[0029]

[Effect of the Invention]Concealment nature, note nature, and a sex with a crack-proof are good, and a carbon copy check etc. can obtain especially a white aliphatic polyester film useful as a display base material which performs printing and a note.

[Translation done.]